

25.06.03

Europäisches  
PatentamtEuropean  
Patent OfficeOffice européen  
des brevets

REC'D 01 AUG 2003

WIPO PCT

## Bescheinigung

## Certificate

## Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

02077783.5

**PRIORITY DOCUMENT**  
SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH  
RULE 17.1(a) OR (b)

Der Präsident des Europäischen Patentamts;  
Im Auftrag

For the President of the European Patent Office  
Le Président de l'Office européen des brevets  
p.o.

R C van Dijk

DEN HAAG, DEN  
THE HAGUE,  
LA HAYE, LE 06/03/03  
EPA/EPO/OEB Form 1014 - 02.91

Best Available Copy



Europäisches  
Patentamt

European  
Patent Office

Office européen  
des brevets

**Blatt 2 der Bescheinigung  
Sheet 2 of the certificate  
Page 2 de l'attestation**

Anmeldung Nr.:  
Application no.: **02077783.5**  
Demande n°:

Anmeldetag:  
Date of filing:  
Date de dépôt: **10/07/02**

Anmelder:  
Applicant(s):  
Demandeur(s):  
**Koninklijke Philips Electronics N.V.**  
**5621 BA Eindhoven**  
**NETHERLANDS**

Bezeichnung der Erfindung:  
Title of the invention:  
Titre de l'invention:  
**Transparent polycrystalline aluminium oxide**

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s) revendiquée(s)

Staat: State: Pays:	Tag: Date: Date:	Aktenzeichen: File no. Numéro de dépôt:
---------------------------	------------------------	---

Internationale Patentklassifikation:  
International Patent classification:  
Classification internationale des brevets:

/

Am Anmeldetag benannte Vertragstaaten:  
Contracting states designated at date of filing: **AT/BG/BE/CH/CY/CZ/DE/DK/EE/ES/FI/FR/GB/GR/IE/IT/LI/LU/MC/NL/**  
Etats contractants désignés lors du dépôt:

Bemerkungen:  
Remarks:  
Remarques:

## Transparent polycrystalline aluminium oxide

The invention relates to highly dense transparent aluminum oxide and structures thereof for applications where, e.g. in the lighting industry, a fine crystal size has to be obtained and stabilised for use at temperatures of 800°C or more. The invention is also related to an electric lamp having a discharge tube with a wall of such ceramic.

5 Sintered transparent alumina ceramics consisting of chemically and thermodynamically stable corundum phase ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) have been available for several decades. Traditionally, they are produced starting from very fine-grained transitional alumina raw powders and obtain a high sintering density by annealing at very high temperatures > 1600°C. As a result, the ceramic microstructures are coarse with crystal sizes typically >

10 15 µm. As a consequence of this coarse microstructure, these materials exhibit even in thin components only translucency but no transparency. Besides the known ceramics have a relative low bending strength, usually less than 300MPa.

Transparency of a ceramic component is herein defined as having a value for real in-line transmission RIT of at least 30%, wherein the real in-line transmission RIT is measured over an angular aperture of at most 0.5° at a sample thickness of 0.8 mm and with a monochromatic wave length of light  $\lambda$ .

In literature it is common practise for optical properties to use total forward transmission (TFT) and in-line transmission (IT), the latter measured with commercially available spectrometers. As these have angular apertures of several degrees the so measured IT includes a large amount of forward scattered light. As a consequence, for scattering samples, both TFT and IT will always result in values much higher than the value of RIT for the same sample. It is not possible to establish any quantitative relationship with the RIT. It is however possible to compare values of real in-line transmission which have been taken at samples with a thickness, which differs from the 0.8mm as defined. For a sample 1 with thickness d<sub>1</sub> and RIT value T<sub>1</sub> and a second sample having a thickness d<sub>2</sub>, the value T<sub>2</sub> of the RIT satisfies the relation

$$T_2 = (1-R) * [T_1 / (1-R)]^{d_2/d_1}$$

(1)

with R the coefficient of surface reflection which is for alumina 0.14 (incorporating the reflection on both surfaces). Due to reflection losses a transmission value, either RIT, TFT or IT cannot exceed a value of 86%.

5 The inventors have established that for a ceramic sample having a very small porosity as well as small pores, at least smaller than 0.01% respectively <100nm the real in-line transmission RIT is correlated to the samples structure. When measured according to the above stated definition the obtained RIT fulfils the expression ,

$$RIT = (1 - R) \exp\left(-\frac{3\pi^2 G d \Delta n^2}{2\lambda_0^2}\right), \quad (2)$$

10 with R the coefficient of surface reflection (for  $\text{Al}_2\text{O}_3$  0.14), d the sample thickness, G the average crystal size,  $\Delta n$  the effective birefringence of alpha-alumina (0.005) calculated as the weighted average of the refractive index differences between each of the main optical axes and  $\lambda_0$  the wavelength of the monochromatic incident light in vacuum. With higher porosity percentages and larger pore sizes, the measured RIT results in significant smaller values than predicted by the above expression.

15 It has been proposed to obtain translucent sintered products with fine crystal sizes of 2-5 $\mu\text{m}$  by applying a slip casting approach in combination with pressureless pre-sintering and hot-isostatic post-densification (HIP). No RIT was measured on a test sample but the maximum IT was 46% (at 1mm sample thickness, visible to infrared light - no wavelength given) observed at an average crystal size of 5 $\mu\text{m}$ .

20 Only slight improvements were observed when the crystal sizes are reduced towards the sub-micrometer range. Dense samples produced with an average crystal size of 0.82 $\mu\text{m}$  by injection moulding, pre-sintering and HIP were reported to have an IT (at 500nm wave length) of 78% recorded at a sample thickness of 0.5mm thickness.

25 The purity of the alumina in these cases was reported to be 99.99%. The mentioned HIP process was done at a temperature of about 1250 to 1280°C giving rise to an additional difficulty, however, when the ceramics are intended for use in a discharge lamp, a discharge tube of such discharge lamp is operated at temperatures ranging from 1100 to 1300°C. Any technical use of these sintered products at temperatures similarly high or even higher than the HIP temperatures will unavoidably coarsen the described highly pure alumina 30 microstructures. Whereas several additives like for instance MgO and ZrO<sub>2</sub> have been reported to retard crystal growth in annealing alumina ceramics, the precise effects are often unclear.

According to EP 1053983 related to translucent polycrystalline ceramics with mean facet lengths no longer than a maximum wave length  $\lambda$  of the light (which for  $\lambda = 600\text{nm}$  e.g. means a crystal size of about  $0.6\mu\text{m}$  since the facet length is about half of the average crystal size), an additive of only  $0.05\text{mol-}\%$   $\text{ZrO}_2$  as a sinter dopant in transparent sintered alumina ceramics has a degenerating effect on both the optical transmittance and the strength and the hardness compared with samples without  $\text{ZrO}_2$ . For  $0.5\text{mm}$  thin discs and  $\lambda < 800\text{nm}$ , the value measured for what is called linear transmission, which in this case can be compared to the real in-line transmission RIT, decreases to 25% compared with 40% measured for a zirconia free microstructure with  $\text{MgO}$  dopant ( $0.1 \text{ mol-}\%$ ). A RIT value of 25% for a thickness  $d$  of  $0.5\text{mm}$  corresponds according to the relation (1) to a value of 12% for thickness  $d=0.8\text{mm}$ . For the zirconia free microstructure the corresponding value for a thickness  $d=0.8\text{mm}$  is 25%.

A transparent  $\text{Al}_2\text{O}_3$  component with a value for the RIT measured over an angular aperture of at most  $0.5^\circ$  at a sample thickness of  $0.8\text{mm}$  and with a monochromatic wave length of light  $\lambda$  of at least 30% having an acceptable strength is therefore unknown. That is a problem. Neither is known a lamp discharge vessel of transparent polycrystalline alumina, of which the small crystal structure is retained over a long period of time of lamp operation circumstances. That is also a problem. It is therefore the objective of the present invention to dissolve the problems and to provide a component, which overcomes the previously mentioned limitations.

The present invention provides a polycrystalline alumina component with an additive which is characterised in that the alumina has an average crystal size  $\leq 2\mu\text{m}$ , and has a relative density higher than 99.95% with a real in-line transmission  $\text{RIT} \geq 30\%$ , preferentially  $> 40\%$  and more preferentially  $> 50\%$ , measured over an angular aperture of at most  $0.5^\circ$  at a sample thickness of  $0.8\text{mm}$  and with a single wave length of light  $\lambda$ , preferably of  $645\text{nm}$ , and that the additive comprises at least one of the substances of the group consisting of  $\text{MgO}$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Er}_2\text{O}_3$  and  $\text{La}_2\text{O}_3$ .

The result that a value of  $\text{RIT} > 30\%$  is obtained and a fine crystal size  $\leq 2\mu\text{m}$  or, preferentially  $\leq 1\mu\text{m}$  is stabilised for longer periods when used at temperatures of  $800^\circ\text{C}$  or more on high temperature annealing, is surprising and clearly is in disagreement with the previous state of the art. It is enabled here by the combination of very small crystal sizes with an extremely high relative density  $> 99.95\%$ , implying a very small residual porosity.

Preferably an alumina component according to the invention is made according to the process described hereafter. An aqueous slurry with a solid loading of

41wt-% was prepared at pH = 9 from TM-DAR corundum powder [average particle size 0.2 $\mu$ m; make Boehringer Ingelheim Chemicals, Japan] without any further additives. A high degree of dispersion was obtained after at least 1 day of ultra sound or at least half a day of wet ball milling, using milling beads that could not give rise to contaminations other than alumina or oxydizable wear. An additive or dope selected from the group formed by MgO, Y<sub>2</sub>O<sub>3</sub>, Er<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub> was then introduced by the addition of pure and finely grained oxide powder of the said dope. The average particle size of the dope or additive is preferably chosen smaller than the alumina crystal size obtained after sintering and HIP treatment. Alternatively the additive or dope can be introduced by a precursor containing one or more of the elements Mg, Y, Er and La. Reference samples without additive were prepared in the same way, except that no dope was added.

The thus obtained suspensions were without further degassing either pressure cast at a pressure of 4 bars using a Millipore hydrophilic membrane with an average pore diameter of 50nm, or slipcast on a porous mould with an average porosity of about 50% and an average pores size of about 100nm. After consolidation the pellets were dried in air for about 4 hours and hereafter further dried in a stove at a temperature of 80°C for 4 more than hours. The dried compacts were calcined at 600°C for 2 hours in pure oxygen to remove pollutants. Hereafter the pallets were sintered at a sinter temperature (Ts) ranging from 1150°C to 1350°C in either oxygen, vacuum or humidified hydrogen (dew point 0°C). Pellets with a density higher than 96% were given a subsequently HIP treatment at a temperature of 1200°C at a pressure of 200Mpa for at least 2 hours. The pellets were ground on both parallel sides, first with successively finer diamond grains of finally 3 $\mu$ m. The final thickness of the discs was 0.8mm.

The real in-line transmission (RIT) of the thus formed samples was measured using a red diode laser with a wavelength  $\lambda$  of 645nm and a detector at a distance from the illuminated sample of at least 1 meter to ensure an angular aperture of 0.5°. Also the total forward transmission (TFT) was measured. In a number of cases the absorption (ABS), the total reflection (TR) and the density after sintering ( $\rho$ ) was measured. The results are shown in Table I.

Table I

MgO (ppm)	Ts (°C)	Sinteratmosphere	RIT	TFT	ABS
133	1200	O <sub>2</sub>	54	76	6
300	1200	O <sub>2</sub>	55	76	6
1000	1220	O <sub>2</sub>	45	72	6
133	1200	H <sub>2</sub>	44	65	17
300	1200	H <sub>2</sub>	46	67	17
1000	1220	H <sub>2</sub>	45	67	16
Y <sub>2</sub> O <sub>3</sub> (ppm)	Ts (°C)	p (%)	RIT	TFT	ABS
100	1245	96.5	61.1	76.1	9.6
	1250	99.2	58.3	77.0	8.4
	1300	100	54.3	76.2	9.2
400	1285	98.2	62.0	75.8	9.9
	1300	99.8	62.4	75.3	10.3
1000	1300	96.5	66.3	73.7	12.2
	1330	99.0	46.1	67.2	16.7
Er <sub>2</sub> O <sub>3</sub> (ppm)_sinteratmosphere	Ts (°C)	p (%)	RIT	TFT	ABS
350_H <sub>2</sub>	1235	97.0	61.0	76.6	9.3
	1280	98.0	57.9	75.4	
	1290	98.4	57.0	75.1	10.7
50 + 300ppm MgO_H <sub>2</sub>	1260	98.3	57.3	76.0	
350_O <sub>2</sub>	1275	97.0	60.6	82.5	
50 + 300ppm MgO_O <sub>2</sub>	1250	98.4	61.0	82.3	2.6
La <sub>2</sub> O <sub>3</sub> Tsinter (°C)_Sinteratmosphere	p (%)	RIT	TFT	TR	AB8
1260_H <sub>2</sub>	98.3	46.1	69.4	15.3	15.3
1290_O <sub>2</sub>	99.0	46.7	76.7	17.7	5.6
1290_air	97.2	53.0	78.3	15.9	5.8

For the examples having  $\text{La}_2\text{O}_3$  as additive the HIP was performed at 1250°C for 6 hours. Influences of annealing treatments (annealing time  $t$  in hours and annealing temperature in °C) on crystal size structure is shown in Table II. The sample indicated Reference in Table II is formed of alumina without an additive or dope.

5

Table II

### Crystal size (micron; $\mu\text{m}$ )

In another experiment done by simulation the longer term influence of increased temperature on the crystal size has been investigated. The simulation is based on the model as disclosed in J. Am. Ceram. Soc. 73(1990) 11, 3292-3301. The effect on samples having a additive of dose of the selected group of oxides is shown in Table III.

5

Table III

Sample and temperature	24 h	100 h	1000 h	10.000 h
600 ppm La <sub>2</sub> O <sub>3</sub>				
1100 °C	0.50	0.50	0.51	0.61
1150 °C	0.50	0.51	0.59	0.98
1200 °C	0.52	0.56	0.88	1.78
1250 °C	0.59	0.77	1.51	3.23
350 ppm Er <sub>2</sub> O <sub>3</sub>				
1100 °C	0.60	0.60	0.62	0.77
1150 °C	0.60	0.62	0.74	1.27
1200 °C	0.63	0.70	1.13	2.31
1250 °C	0.73	0.98	1.94	4.15
100 ppm Y <sub>2</sub> O <sub>3</sub>				
1100 °C	0.57	0.57	0.60	0.76
1150 °C	0.58	0.59	0.76	1.38
1200 °C	0.61	0.70	1.22	2.54
1250 °C	0.74	1.04	2.13	4.56
300 ppm MgO + 50 ppm Er <sub>2</sub> O <sub>3</sub>				
1100 °C	0.54	0.54	0.57	0.76
1150 °C	0.55	0.56	0.72	1.31
1200 °C	0.58	0.67	1.16	2.42
1250 °C	0.71	0.99	2.03	4.35

Resulting values for the RIT after 24 hours annealing treatments is shown in Table IV. The annealing treatments were done at different temperatures as indicated in °C.

Table IV

Dope (ppm)	After HIP	1250°C	1275°C	1300°C
100 Y <sub>2</sub> O <sub>3</sub>	58	54		38
1000 Y <sub>2</sub> O <sub>3</sub>	66	68		61
350 Er <sub>2</sub> O <sub>3</sub>	57	54		42
300 MgO + 50 Er <sub>2</sub> O <sub>3</sub>	56	51		33
La <sub>2</sub> O <sub>3</sub>	46	39		28
1000 MgO	46	33		
133 MgO	44	35		
Reference	45		19	

The sample indicated as Reference in Table IV is formed of alumina without an additive or dope.

5 Examples of discharge lamps having a discharge tube made of alumina according to the invention are described with reference to a drawing. The drawing shows a lamp 10 with discharge tube 1 having a ceramic wall 2 of transparent ceramic according to the invention. The lamp is provided with a partly broken away outer bulb 11. The discharge tube of the lamp is provided with electrodes 60, 70, which are connected by a known in the art leadthrough constructions 6, 7 to current conductors 13, 14. The current conductors are connected on conventional way with electric contacts of a lamp base 12. In a first example the discharge tube was made by slip casting of a slurry prepared according to the process as described, with 200 ppm La<sub>2</sub>O<sub>3</sub>. The thus formed lanthanum containing shaped body was sintered at a sinter temperature of 1350°C during 2 hours, after which it was given an HIP treatment for 24 hours at a temperature of 1250°C.

In a second example the discharge tube was made by slip casting of a slurry prepared according to the process as described, with 300 ppm MgO. The thus formed magnesium containing shaped body was sintered at a sinter temperature of 1220°C during 2 hours, after which it was given an HIP treatment for 24 hours at a temperature of 1150°C.

20 The thus formed discharge tubes each have a ceramic wall with an average crystal size of 0.5 to 0.7 µm. In both examples of discharge tubes the ceramic wall material showed a value for the RIT of at least 60%.

## CLAIMS:

1. Polycrystalline alumina component with an additive characterised in that the alumina has an average crystal size  $\leq 2\mu\text{m}$ , and has a relative density higher than 99.95% with a real in-line transmission RIT  $\geq 30\%$  measured over an angular aperture of at most  $0.5^\circ$  at a sample thickness of 0.8mm and with a single wave length of light  $\lambda$  and that the additive comprises at least one of the substances of the group consisting of MgO, Y<sub>2</sub>O<sub>3</sub>, Er<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub>.  
5
2. Polycrystalline alumina component according to claim 1, characterised in that the additive is present in an amount of at least 10ppm.  
10
3. Polycrystalline alumina component according to claim 1 or 2, characterised in that the additive is Y<sub>2</sub>O<sub>3</sub> in a quantity of at least 50ppm and at most 1000ppm.  
15
4. Polycrystalline alumina component according to claim 1 or 2, characterised in that the additive contains Er<sub>2</sub>O<sub>3</sub> in a quantity of at least 50ppm and at most 5000ppm.  
20
5. Polycrystalline alumina component according to claim 1 or 2, characterised in that the additive is La<sub>2</sub>O<sub>3</sub> in a quantity of at least 100ppm and at most 5000ppm.  
25
6. Polycrystalline alumina component according to claim 1 or 2, characterised in that the additive is MgO in a quantity of at least 100ppm and at most 1000ppm.
7. Discharge lamp characterized in that the lamp is provided with a discharge tube having a wall of ceramic as claimed in any of the preceding claims.
8. Lamp according to claim 6 characterized in that the discharge tube has an ionisable filling containing a metal halide.

10

10.07.2002

9. Method to form a polycrystalline alumina component as claimed in one of the preceding claims characterized in that the process includes the steps of

- preparing a slurry of corundum power with a mean grain size  $\leq 0.2\mu\text{m}$ ,
- addition of a dopant, selected from a group formed by precursors containing one or more of the elements Mg, Y, Er and La and oxides of the set  $\text{MgO}$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Er}_2\text{O}_3$  and  $\text{La}_2\text{O}_3$ ,
- casting the slurry in a mould,
- drying and sintering of the thus form shaped body, and
- performing a HIP treatment at a temperature of at least  $1150^{\circ}\text{C}$  for at least 2 hours.

10 10. Method according to claim 6, 7 or 8 wherein the prepared slurry after the addition of the dopant is slip cast in a mould.

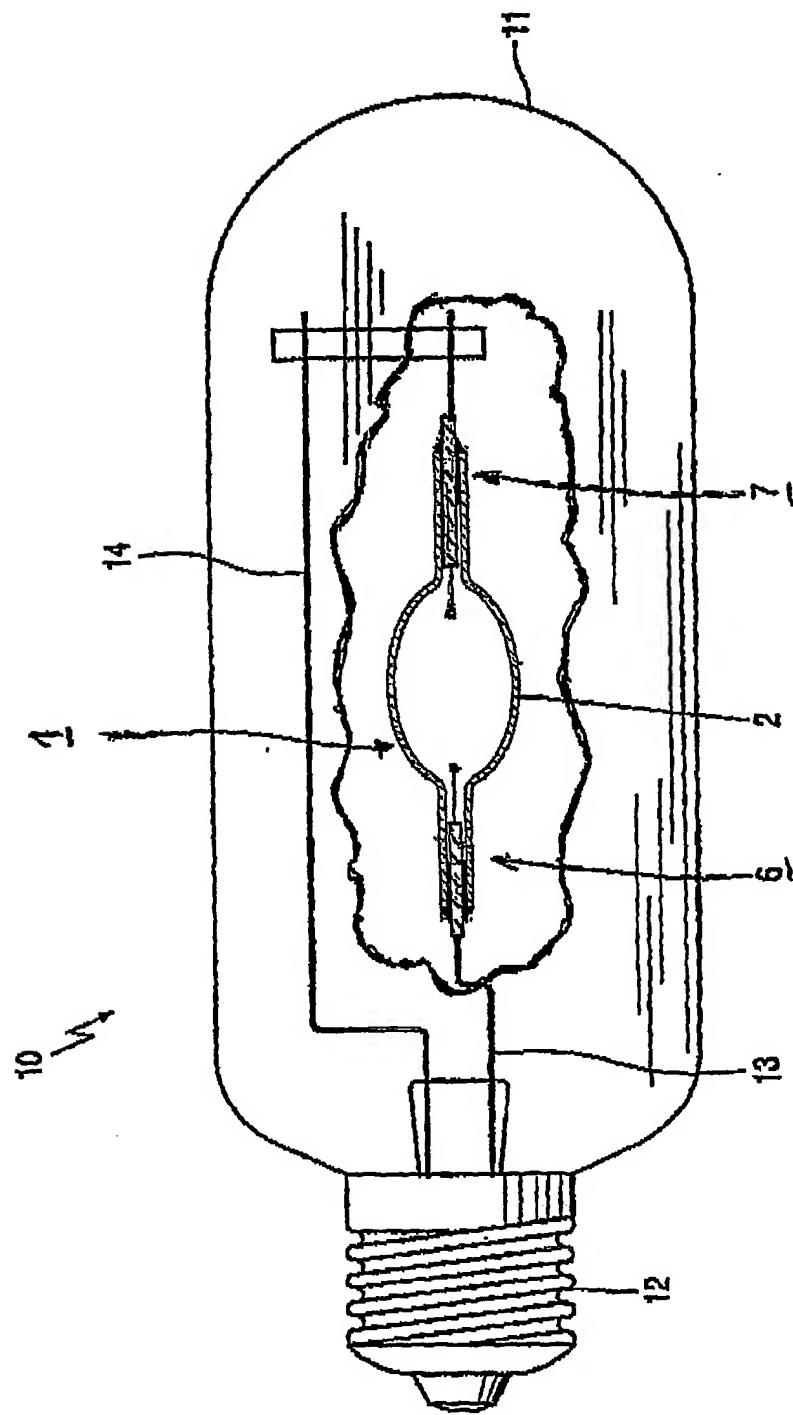
**ABSTRACT:**

The invention relates to highly dense transparent aluminum oxide (alumina) and structures thereof for applications where, e.g. in the lighting industry, a fine crystal size has to be obtained and stabilised for use at temperatures of 800°C or more. The invention is also related to an electric lamp having a discharge tube with a wall of such ceramic.

5       The alumina according to the invention is provided with an additive and has an average crystal size  $\leq 2\mu\text{m}$ , and has a relative density higher than 99.95% with a real in-line transmission RIT  $\geq 30\%$ , preferentially  $> 40\%$  and more preferentially  $> 50\%$ , measured over an angular aperture of at most 0.5° at a sample thickness of 0.8 mm and with a single wave length of light  $\lambda$ , preferably of 645nm, and that the additive comprises at least one of the  
10 substances of the group consisting of MgO, Y<sub>2</sub>O<sub>3</sub>, Er<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub>.

Fig. 1

1/1



**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**